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Preliminary Results of the Comparison of the Electrochemical Behavior of a Thioether and Biphenyl

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UTTL: Preliminary results of the comparison of the electrochemical behavior of a thioether and biphenyl

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ABA: E.A.K.

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PRELIMINARY RESULTS OF THE COMPARISON OF THE
ELECTROCHEMICAL BEHAVIOR OF A THIOETHER
AND BIPHENYL

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ABSTRACT

An electrochemical cell was constructed to explore the feasibility of using electrochemical techniques to simulate the tribochemistry of various substances. The electrochemical cell was used to study and compare the behavior of a thioether [1,3-bis(phenylthio) benzene] and biphenyl. Under controlled conditions biphenyl undergoes a reversible reduction to a radical anion whereas the thioether undergoes an irreversible reduction yielding several products. These results are discussed in relationship to boundary lubrication.

INTRODUCTION

The C-ethers are aromatic compounds (basically thioethers) developed as possible liquid lubricants useful to 260° C (ref. 1). They are thermally stable to 390° C (from isoteniscope measurements) and oxidatively stable to 260° C. They have a -29° C pour point, low vapor pressure, and a high surface tension. Some of their drawbacks include poor boundary lubricating ability and poor wetting characteristics. Another drawback of the C-ethers is the high wear obtained and the excessive formation (under boundary lubricating conditions) of an insoluble deposit. The high wear and deposit formation is especially prevalent when lubricating conditions are taking place in a low oxygen, low moisture environment.

The presence of oxygen or moisture in the fluid environment improves the boundary lubricating properties of polynuclear aromatics (ref. 2). Goldblatt (ref. 3) proposed a radical anion model to explain the lubricating behavior of polynuclear aromatic fluids. Although the C-ethers are not polynuclear aromatic fluids (i.e. fused ring aromatics), their lubricating behavior is similar to that of the polynuclear aromatics. It was this similarity that led to the idea of using an electrochemical cell to investigate the possibility of using this method to study and compare the chemical behavior of the C-ethers with that of polynuclear aromatics.

The objective of this study was to assess whether the excessive wear and deposit formation associated with the use of C-ethers as a boundary lubricant is due to the presence of radical anions as has been postulated for polynuclear aromatics.

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Background

Several studies using the C-ethers as liquid lubricants have been conducted. In one study a vane pump loop was used to determine the lubricating characteristics of the C-ethers (ref. 4) under a nitrogen atmosphere. After 32 hours of operation, the test was halted due to pump pressure loss. Deposit formation had jammed the pump vanes and rotor and caused high pressure drops across system filters.

In another study (ref. 5), a ball on disk sliding friction apparatus was used to investigate the lubricating characteristics of the C-ethers. It was found that greater quantities of a deposit (referred to as "friction polymer") was formed in a low oxygen atmosphere. This is illustrated by Ferrographic analysis of a used C-ether tested in nitrogen (fig. 1a) and air (fig. 1b).

Clark and Miller (ref. 1), evaluated formulated C-ethers, using bench and bearing tests, as liquid lubricants useful to 260° C. All C-ether formulations tested resulted in extreme cage wear and excessive deposit problems. The excessive deposits caused repeated filter pluggings.

These studies verify that the lubricating behavior of the C-ethers is similar to that of polynuclear aromatic fluids. Appeldoorn and Tao (ref. 2) studied the lubricating behavior of heavy aromatic liquid lubricants (most of them polynuclear aromatics) and reported that these fluids, in the absence of oxygen (argon atmosphere, < 0.005 percent oxygen) and moisture (< 20 p.p.m.) caused extreme wear (the authors called it "scuffing") at low loads. They also observed that the presence of small amounts of oxygen or moisture decreased this wear. They pointed out that this is in contrast to the behavior of alkanes (non-aromatics) where high wear occurs in the presence of oxygen and moisture. Appeldoorn and Tao listed three explanations to account for the behavior of aromatic fluids, but rejected all because the explanations could not account for all the observations.

Goldblatt examined the problem (ref. 3) and theorized that the behavior of polynuclear aromatics could be accounted for if these fluids formed radical anions at a rubbing surface. Figure 2 outlines the radical anion model Goldblatt proposed. During boundary lubrication nascent metal surfaces are continuously formed. An aromatic molecule is then adsorbed onto a nascent metal surface and electron transfer occurs from the metal surface to the aromatic molecule. The aromatic molecule then desorbs from the metal surface as a radical anion. In the absence of oxygen and moisture, the radical anion can attack the surrounding metal (or metal oxide) leading to accelerated wear. The radical anion, on the other hand, can be quenched by oxygen or moisture.

Goldblatt's theory was proposed only for polynuclear aromatics, where these compounds are known to form radical anions under controlled conditions (ref. 6). The C-ethers, although polyaromatic, are not polynuclear but their lubricating behavior is similar to the polynuclear aromatics.

A common method for the generation of radical anions is the chemical reagent method, where an aromatic is contacted with sodium metal in the presence of a polar solvent, such as tetrahydrofuran or 1, 2 - dimethoxy ethane (ref. 7). Goldblatt used this method in his studies.

Radical anions, however, can be generated more easily and effectively by electrochemical means. Many researchers have used this electrochemical method in conjunction with electron spin resonance spectroscopy (e.s.r.) to study radical anions (refs. 8, 9).

APPARATUS

Electrochemical Cell

The electrochemical cell used in this study is shown in figure 3. It consists of two pyrex glass compartments, a cathode compartment and an anode compartment, separated by a Teflon membrane. A pool of mercury (0.5 ml) sits at the bottom of the cathode compartment and the cell is filled with 20 ml of a conducting solution. A platinum foil serves as the anode electrode and the pool of mercury serves as the cathode electrode. A platinum wire is used to make electrical contact between the mercury and a D.C. power source. A mercury pool is used in order to obtain a large electrode area. The cell has a gas inlet and outlet enabling one to carry out experiments under nitrogen or air atmospheres.

Liquid Chromatograph

A Waters Model 244 liquid chromatograph was used. The unit is combined with an ultraviolet (UV) absorbance detector and a differential refractive index detector (RI). The UV detector monitors the absorbance at a wave-length of 254 nanometers at sensitivities ranging from 0.005 to 2.0 absorbance units full scale (AUFS). The refractometer is sensitive to all compounds that differ in refractive index from the mobile phase. It will detect changes in the RI as small as 10^{-7} RI units throughout the RI range of 1.00 to 1.75.

TEST PROCEDURE

Electrochemical Cell

Before each test, the two glass compartments of the electrochemical cell were cleaned by rinsing first with chloroform and then methanol. They were then placed into an oven (120° C) and dried overnight. Both electrodes were constructed by inserting a platinum wire through a rubber stopper (fig. 3). The cathode stopper was then inserted into the outer ground glass joint of the cathode glass compartment. A small volume of mercury (0.5 ml) was then injected into the cathode compartment. The mercury forms a pool covering the small length of platinum wire protruding from the stopper.

The conducting solution used for these tests was a 0.1 M solution of tetrapropyl-ammonium perchlorate (TRAP) in acetonitrile. The solution was prepared by dissolving 0.4 grams of the perchlorate in 20 ml of acetonitrile. All chemicals were of reagent grade purity. Next, 0.25 grams of the aromatic sample (under study) was dissolved in the solution. This solution was then introduced into the electrochemical cell. The anode stopper was then inserted into the outer ground glass joint of the anode compartment, and a nitrogen line connected to the gas inlet. A continuous flow rate of nitrogen purged the cell of any air.

The positive potential of a DC power supply was connected to the anode platinum wire and the negative potential to the cathode platinum wire. All tests were conducted by turning on the DC power supply and increasing the voltage in increments of 2 volts up to a maximum 10 volts. At test conclusion, the power supply was turned off and samples were collected from the cell for chromatographic analysis (HPLC).

Sample Preparation for Chromatographic Analysis

The acetonitrile solvent in the samples withdrawn from the electrochemical cell was evaporated to dryness on an evaporating dish. Each sample was then reconstituted with 5 ml of chloroform or heptane depending on which type of chromatographic separation was used. A 100 μ l sample was injected into the chromatograph.

RESULTS

Biphenyl

Biphenyl (fig. 4) is a nonpolynuclear aromatic which can be reduced, using the chemical reagent method, to a stable radical anion (ref. 6). An electron from the sodium metal is transferred from the sodium to the biphenyl molecule where it is delocalized about the biphenyl molecule.

Because of its known radical anion forming property, biphenyl was used as the reference sample in the electrochemical cell. After the cell was prepared and purged with nitrogen, the power supply was connected to the cell. The voltage to the cell was slowly increased (~ 1 minute intervals) in 2 volt increments until an intense blue color started to form above the mercury surface. This occurred at 10 volts (3.5 mA). All aromatics which are reduced to stable radical anions, either chemically or electrolytically, are deeply colored; i.e. the naphthalene radical anion is green, the anthracene radical anion is blue, and the benzonitrile radical anion is red-orange (ref. 7).

The power supply was left at 10 volts for one hour. With continued nitrogen purge, the power supply was disconnected and the blue color immediately disappeared. Then the contents of the cathode compartment were collected and a sample prepared for HPLC analysis.

Figure 5 is the HPLC chromatogram of biphenyl standard. Figure 6 is the chromatogram of the electrolyzed biphenyl sample collected from the cell. It reveals a single peak with a retention time of 6.96 minutes compared to the biphenyl standard retention time of 7.05 minutes. This is within the calibration accuracy of the system (0.1 min.). This indicates no change in composition.

C-ethers

The C-ethers (fig. 7) are a mixture of four nonpolynuclear aromatics. One of the four components (the three phenyl ring component (d) 1,3-bis(phenylthio) benzene) was used as the test sample in the electrochemical cell in order to simplify results.

After preparing the cell, the power supply voltage was again increased in 2 volt intervals. At 10 volts a bright red color started to form over the mercury surface. The voltage was maintained at 10 volts for one hour. Then the power supply was disconnected, but unlike the biphenyl sample, the red color did not disappear. The cell was not disturbed in order to determine the persistence of the red color. At the end of three hours the color was still intense. Then a sample of the colored solution was taken for HPLC analysis. Using a long tip syringe about 5 ml of the cathode contents were withdrawn. But as the red solution entered the syringe chamber (which contained air) the color disappeared. This sample was prepared for HPLC analysis.

Figure 8 is the chromatogram of the three phenyl ring C-ether standard. Figure 9 is the HPLC chromatogram of the sample collected from the cathode compartment; in addition to the original C-ether peak, two other peaks are detected.

A size exclusion analysis of the collected cathode sample was also performed. Figure 10 is the size exclusion chromatogram of the pure three ring C-ether standard. Figure 11 is the size exclusion chromatogram of the electrolyzed sample from the cathode compartment; in addition to the peak for the three ring C-ether, three other peaks are detected (one of lower molecular weight than the original C-ether and three of greater molecular weight).

DISCUSSION

Biphenyl

The electrochemical reduction of biphenyl yielded a radical anion (fig. 12) which exhibited an intense blue color. The blue color disappeared as soon as the voltage to the cell was turned off; presumably, the biphenyl radical anion reversibly oxidized back to the neutral biphenyl molecule. HPLC analysis verified this reaction of the biphenyl radical anion by detecting only the original biphenyl peak.

C-ether

The electrochemical reduction of the three ring C-ether, however, yielded different results. Instead, the C-ether reacted to produce a product or products exhibiting an intense red color which did not disappear after the voltage to the cell was turned off; however, as soon as the product contacted air (the air in the syringe), the red color disappeared. HPLC analysis revealed that the reduced C-ether produced a number of reaction products.

These results may be explained if one assumes that the C-ether is reduced to a radical anion (fig. 13) but that this species decomposes to produce a stable free radical or radicals. The persistence of the red color after the voltage to the cell is turned off, and the disappearance of the red color when the cathode sample is contacted with air is evidence of this possibility. These observations are in accordance with the classical Gomberg free radical experiment (ref. 10), where he prepared a triphenylmethyl free radical (in a benzene solution) exhibiting a yellow color, but as soon as the solution came into contact with oxygen, the yellow color disappeared.

Electron Paramagnetic Resonance

Further supporting evidence for the formation of stable radical species is shown in figure 14. Here an electron paramagnetic resonance (EPR) spectrum of the electrolyzed three ring C-ether is shown. EPR is a technique which detects unpaired electrons and thus free radicals.

In this experiment, a sample of the red solution from the cathode compartment of the electrochemical cell was carefully withdrawn (under a nitrogen atmosphere). The sample was placed in an EPR cell and the spectrum of figure 13 obtained.

This spectrum indicates the presence of two stable free radicals (labeled A and B). Radical B appears as a 1:1 doublet with a splitting of about 250 Gauss. Radical A appears as a 1:2:1 triplet pattern with a splitting of approximately 40 Gauss.

Both are relatively stable species as another spectrum taken one hour later reveals the same pattern. However, radical A had diminished more than radical B, indicating that it is somewhat less stable. Figure 15 shows a possible initial decomposition of the radical anion species which subsequently reacts to produce stable radical species. The structure of these stable species is unknown at this time. However, radical B which has a very large hyperfine splitting is very unusual.

The formation of a stable radical species from a structurally similar aromatic lubricant has been reported. An isomeric mixture of five ring polyphenyl ether components yielded a stable free radical under oxidizing conditions (ref. 11).

HPLC Analysis

As indicated, the HPLC analysis showed the presence of several products. The size exclusion chromatogram indicated both a lower and three higher molecular weight products were formed. Based on calibration standards, these new peaks in the spectrum correspond to two, four, five and possibly six ringed species.

In fig. 16, three possible reaction sequences are shown that would produced lower and higher molecular weight species differing by 6 carbon units (i.e. benzene ring). Reaction 4 is the formation of diphenyl sulfide by abstraction of a proton from the solvent acetonitrile (CH_3CN). Reaction 5 is a coupling reaction of the diphenyl sulfide radical. Reaction 6 is a similar reaction of a three and two ringed species. Further analyses is required to verify these reactions.

Boundary Lubrication

The discussion in the background section of this paper strongly indicates that the C-ether class of lubricants behaves according to the Goldblatt (ref. 3) polynuclear aromatic radical anion model. The preliminary results from an electrochemical cell reported herein support that theory; that is, radical anions are produced that subsequently decompose or react with their surroundings to produce a variety of products. These products (some of higher and one of lower molecular weight) are qualitatively similar to the products produced by a C-ether lubricant from micro-oxidation and high temperature bearing tests (ref. 12).

These preliminary results indicate that the boundary lubrication chemical behavior of aromatic lubricants (such as the C-ethers) may be simulated in an electrochemical cell. Continuing studies will concentrate on determining the chemical structure of the various C-ether reaction products. In addition, inhibitors will be studied in an attempt to mitigate the deleterious reactions.

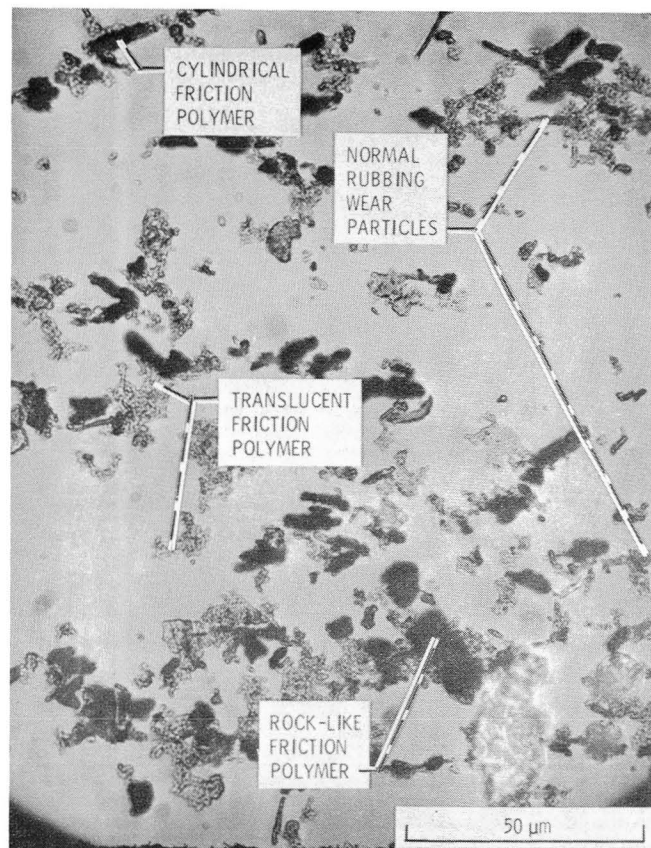
SUMMARY OF RESULTS

The electrochemical behavior of biphenyl and a C-ether lubricant component [1,3 bis(phenylthio) benzene] has been studied. An electrochemical cell was used in conjunction with high performance liquid chromatography (HPLC) and electron paramagnetic resonance (EPR). These preliminary results may be summarized as follows:

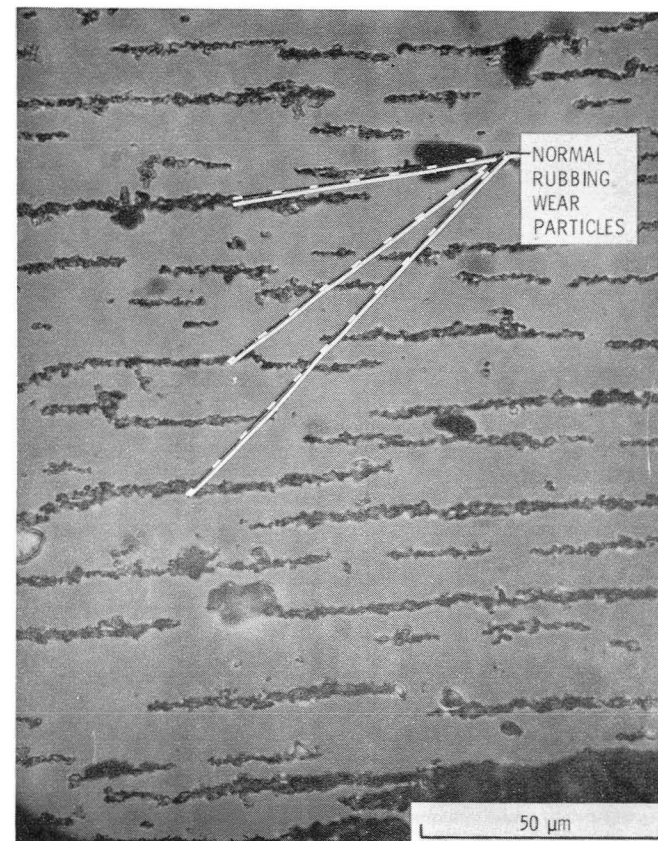
1. Biphenyl yields a radical anion at the cathode in an electrochemical cell which is completely reversible.
2. A C-ether component [1,3 bis(phenylthio) benzene] yields two stable free radicals and a number of other products under identical conditions.
3. The C-ether products which are possibly the result of radical anion decomposition and/or reaction are qualitatively similar to those products generated in micro-oxidation and high temperature bearing tests.
4. It appears that electrochemical cell techniques may be useful for simulating the boundary lubrication chemical behavior of aromatic lubricants.

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(a) Dry nitrogen.



(b) Dry air.

Figure 1. - Photomicrographs of wear debris generated by a C ether at 100⁰ C in dry nitrogen (ref. 5).

1. Metallic surface $\xrightarrow{\text{sliding}}$ nascent metal surface (NMS)
2. NMS + aromatic (ARO) \longrightarrow NMS : ARO (adsorbed aromatic on metal)
3. NMS : ARO \longrightarrow NMS⁺ : ARO⁻ (adsorbed radical anion)
4. NMS⁺ : ARO⁻ \longrightarrow NMS⁺ + ARO⁻ (desorbed radical anion)
5. ARO⁻ + metal or metal oxide \longrightarrow reduced metal oxides or abrasives
6. ARO⁻ + H₂O \longrightarrow ARO-H[•] + OH⁻ \longrightarrow dihydronaphthalene
7. ARO⁻ + O₂ \longrightarrow ARO + O₂⁻ \longrightarrow peroxides \longrightarrow acids or resins
8. ARO⁻ + aliphatic \longrightarrow higher molecular weight products
9. ARO⁻ + aliphatic + O₂ \longrightarrow peroxides (of aliphatics) \longrightarrow acids (of aliphatics) or resins

Figure 2. - Radical anion model.

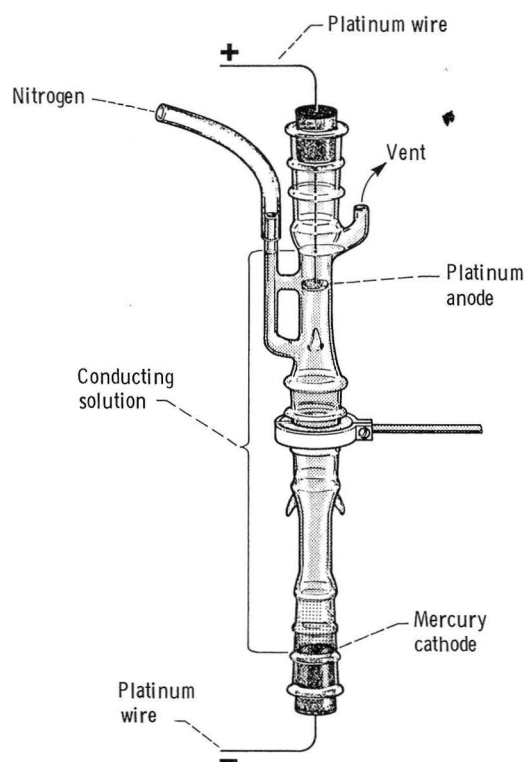


Figure 3. - Electrochemical cell.

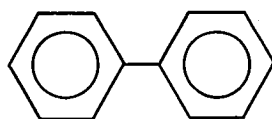


Figure 4. - Biphenyl.

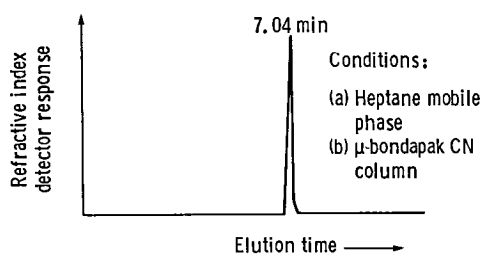


Figure 5. - HPLC (normal phase) chromatogram of biphenyl standard.

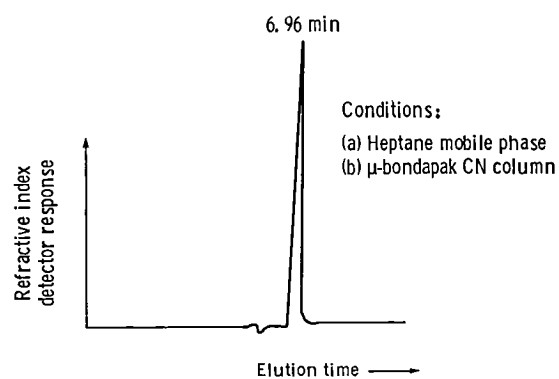
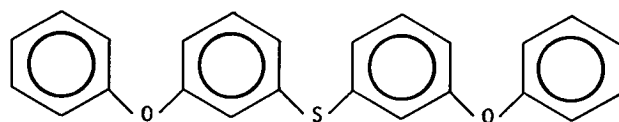
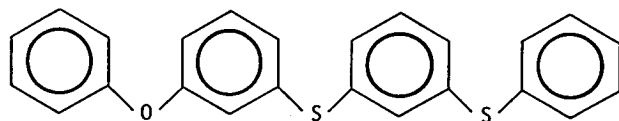


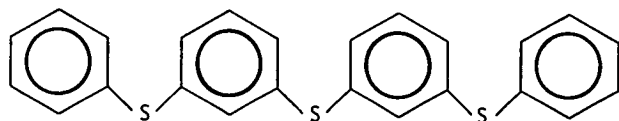
Figure 6. - HPLC (normal phase) chromatogram of electrolyzed cathode sample (biphenyl).



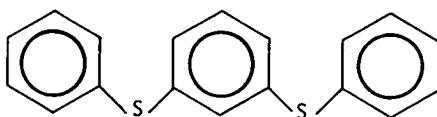
(a) 1,1-thiobis [3-phenoxybenzene]; molecular weight, 370.



(b) 1-phenoxy-3-[3-(phenylthio) phenyl] thio] benzene; molecular weight, 386.



(c) 1,1-thiobis [3-(phenylthio) benzene]; molecular weight, 402.



(d) 1,3-bis (phenylthio) benzene; molecular weight, 294.

Figure 7. - Chemical components of C-ether base fluid.

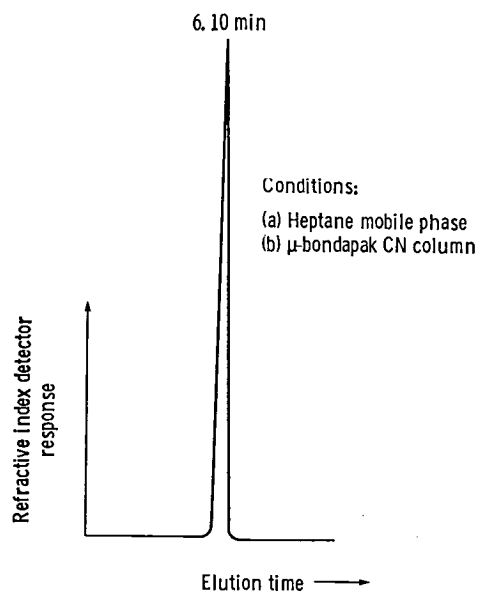


Figure 8. - HPLC (normal phase) chromatogram of three-ring thioether standard.

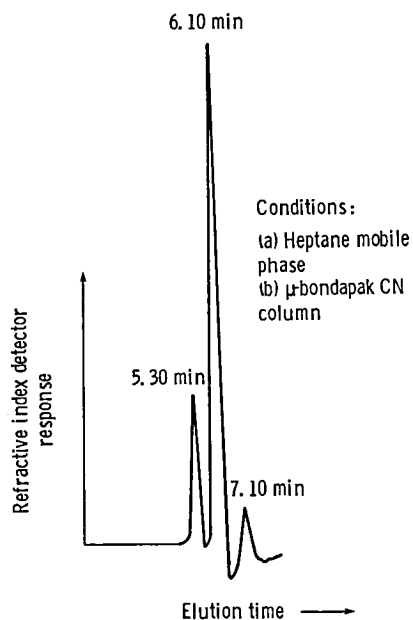


Figure 9. - HPLC (normal phase) chromatogram of electrolyzed sample (three-ring thioether) from cathode compartment.

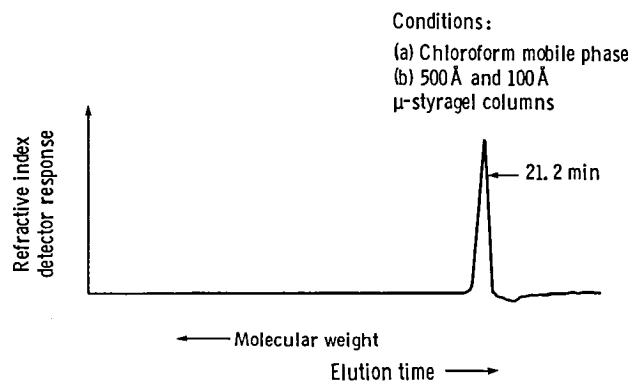


Figure 10. - Size exclusion analysis of the three-ring thioether.

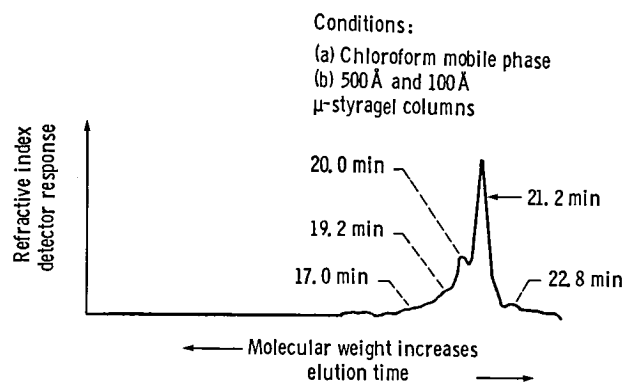


Figure 11. - Size exclusion analysis of electrolyzed cathode sample (three-ring thioether),

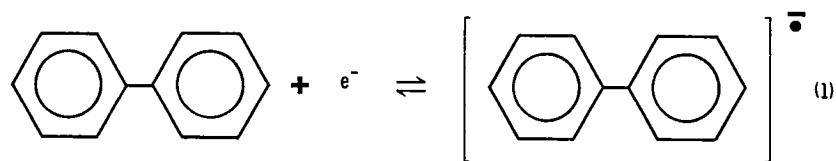


Figure 12. - The electrochemical reduction of biphenyl.

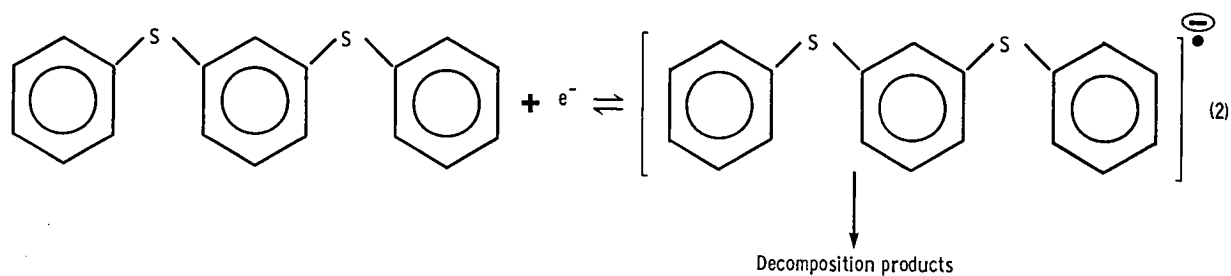


Figure 13. - The electrochemical reduction of the three ring thioether.

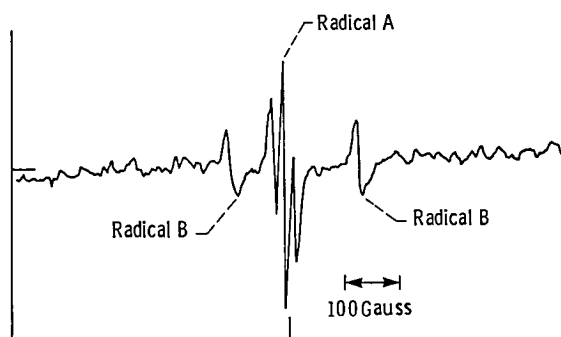


Figure 14. - EPR spectrum of a three ring thioether from electrochemical cell.

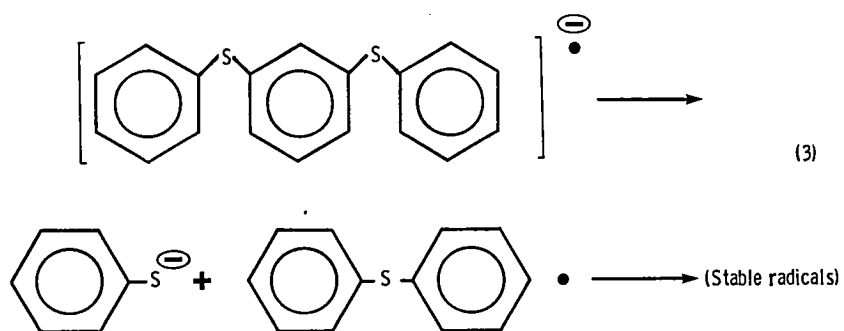


Figure 15. - Possible decomposition reaction of three-ring thioether radical anion.

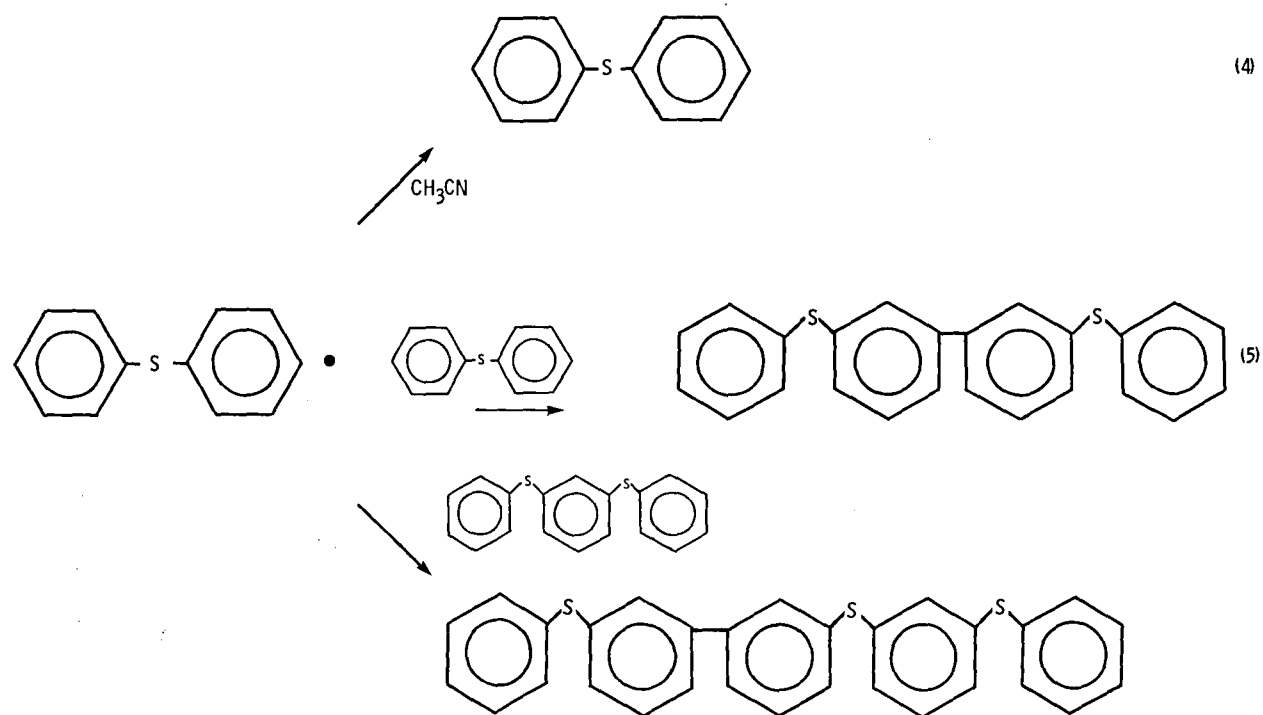


Figure 16. - Possible reactions of thioether decomposition product.

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